

Does Ozone Carryover Affect Day-of-the-Week Phenomena?

For this to be true, carryover of ozone, apparent in changes of ozone concentrations aloft from one day to the next, should experience day-of-the-week variations. Without the impact of ozone layers aloft, ozone concentrations at ground level should decline from previous day's level. Two-day old ozone layers aloft should impact ground level ozone concentrations. We report evidence of these three phenomena.

During the 1997 Southern California Ozone Study (SCOS97-NARSTO), we operated a Dasibi 1003-AH ultra-violet photometry ozone analyzer at the Atlantic Richfield Company (ARCO) headquarter tower in central Los Angeles [198 meters mean sea level (msl), roughly 90 meters above ground level (agl)]. On July 18, 1997, ARB audit team invalidated these data because the temperature of the analyzer compartment was not recorded, data logger was inoperative, and the inlet was not 1 meter away from the building; analyzer deviated by 8% from the true value. For these reasons, the data did not meet federal Environmental Protection Agency (EPA) guidelines. ARB has tested these ozone analyzers at very high temperatures confirming they would not produce erroneous data; we thus have confidence in ARCO tower ozone data. The South Coast Air Quality Management District operates a routine monitoring site located inside a Los Angeles Department of Water and Power facility on North Main Street (LANM). LANM data have met the federal EPA quality guidelines. The ARCO tower is roughly 1 mile west south west of LANM. The data from these two sites provide a rough but continuous idea of the shallowest portion of ozone layers aloft.

During SCOS97-NARSTO, balloons with potassium iodine total oxidant instruments, and temperature and relative humidity capacitance probe were launched from seven locations. University of Southern California's (USC) Hancock Foundation Building located south of Central Los Angeles was one site location. Balloons were launched at 0200, 0800, 1400, and 2000 hour local time. The USC site is located 4 miles south west of LANM. The USC data provides a snapshot in time view of the entire ozone layers aloft. The USC ozone balloon data have passed "level I" quality guidelines (Fujita et. al., 1999).

In Figure 1, on average ARCO tower ozone is greater than LANM by 10 parts per billion volume (ppbV). 75th percentile values are significantly above the average and there are negative 25th percentile values. These differences are not merely due to differences in measuring instruments and indicative of movement of ozone layers downwards or scavenging by local nitrogen oxides.

Table 1 indicates that ozone concentrations at ARCO have a different relationship from day to day than at LANM. The difference between ARCO and LANM has a relationship more like that of ARCO and less like that of LANM but yet different from both. There are indications that even 100 meters, the ozone aloft has a different profile than at ground level. Moreover, observation of day-to-day couples suggests that such relationships for Friday-Saturday and Sunday-Monday are significantly weaker than the day-to-day couple before and after. This is consistent with carryover on Fridays to

mostly contribute to Saturday and Sunday ozone concentrations and be exhausted by Monday.

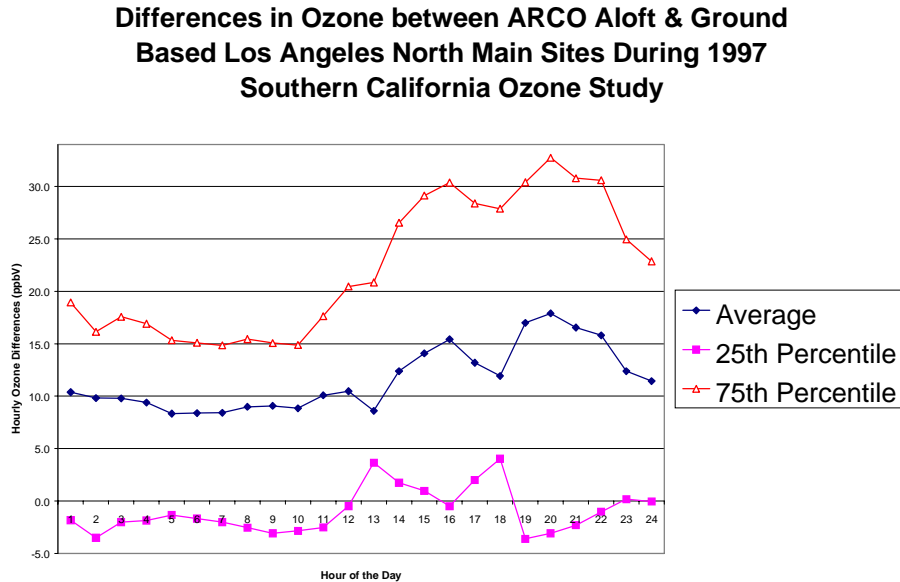


Figure 1. Statistical Parameters of Ozone Concentration Differences between ARCO and LANM

All Day-Pairs of the differences between ARCO & LANM during SCOS97-NARSTO	ARCO	LANM
Correlation Coefficient		
THURSDAY-FRIDAY	0.67	0.80
FRIDAY-SATURDAY	0.49	0.69
SATURDAY-SUNDAY	0.73	0.87
SUNDAY-MONDAY	0.58	0.68
MONDAY-TUESDAY	0.79	0.81
TUESDAY-WEDNESDAY	0.55	0.64
WEDNESDAY-THURSDAY	0.53	0.78

Table 1. Correlation Coefficient for all Day-to-Day couples of ARCO-LANM ozone data

To further investigate this influence during SCOS97-NARSTO, we reviewed how ARCO-LANM difference for each day were related to the next (Table 2). Versions of Table 2 for ARCO and LANM have been created and express much stronger day-to-day relationships similar to values noted in Table 1. Table 2 squares indicate the extent of changes that ozone aloft profile (within 100 meters) experienced from one day to the next. Lightly shaded squares ($R^2=0.01$ to 0.03) suggest significant changes of ozone aloft profile. These are mostly confined to Sunday to Monday and Friday to Saturday, when as previously, changes in ozone aloft are different from other days (Table 1). Darkly shaded squares ($R^2=0.8$ to 0.9) suggest significant continuation of ozone aloft profiles. These are spread throughout the days of the week. Carryover depends on continuation of ozone aloft profiles to build stronger aloft layers; significant changes in aloft layers may signal exhaustion of aloft layers. Building of stronger aloft layers does not seem to vary

by day of the week. But, exhaustion of ozone layers aloft has a strong day-of-the-week variation.

Multi R for Relationship between Daily ARCO-LANM Differences							
Week	Thr-Fri	Fri-Sat	Sat-Sun	Sun-Mon	Mon-Tue	Tue-Wed	Wed-Thr
3-Jul		0.29	0.18	0.01	0.26	0.84	0.35
10-Jul	0.34	0.14	0.31	0.14	0.48	0.17	0.30
17-Jul	0.23	0.39	0.01	0.36	0.07	0.30	0.67
24-Jul	0.12	0.09	0.14	0.10	0.68	0.09	0.52
31-Jul	0.68	0.32	0.45	0.39	0.68	0.52	0.14
7-Aug	0.28	0.48	0.27	0.43	0.71	0.35	0.03
14-Aug	0.22	0.01	0.14			0.60	0.60
21-Aug					0.78	0.75	0.60
28-Aug	0.66	0.67	0.64	0.91	0.85	0.66	0.79
4-Sep	0.81	0.58	0.56	0.33	0.57	0.51	0.56
11-Sep	0.59	0.40	0.62	0.86	0.38	0.90	0.44
18-Sep	0.71	0.43	0.85	0.78	0.63	0.23	0.52
25-Sep		0.51	0.65	0.13	0.86	0.74	0.61
2-Oct	0.40	0.32	0.10	0.69	0.89	0.79	0.13
9-Oct	0.50	0.18	0.31	0.60	0.48	0.73	0.85
16-Oct		0.01	0.31				

Table 2. Correlation of Hourly ARCO-LANM Differences for Day-to-Day Couples

This day-to-day couples analysis however leaves the connection to the magnitude of the ground level changes unexplored. To explore these changes, we assembled maximum hourly daily concentrations for the LANM site during SCOS97-NARSTO. Sunday was the highest ambient ozone day of the week at the LANM site during SCOS97-NARSTO. We note significant changes from ozone highs (>80 ppbV - red) to lows (60 ppbV or less - blue) in Table 3. Such changes are rare (4) and occur Sunday to Monday (2) and Tuesday to Wednesday (2). The most extreme of these day-to-day changes (>50 ppbV-underlined) coincide with very low correlation between day-to-day ozone aloft profiles (0.01, 0.23, and 0.13 R^2 in order of appearance in Table 3). Exhaustion of ozone layers aloft, expressed in weak day-to-day ozone aloft correlations, coincides with extreme changes in day-to-day ozone. Two out of three such occasions occur on Sunday to Monday.

Reductions of 30 ppbV or more from one day to the next occurred from Sunday to Monday (5), Monday to Tuesday (1), Tuesday to Wednesday (1), and Wednesday to Thursday (1). No such reduction occurred from Thursday through Sunday. Sunday to Monday correlations were either high (R^2 of 0.8 or higher) or low (0.13 or 0.01). Other days of the week have moderate correlations (R^2 of 0.52, 0.61, and 0.63). The high R^2 may indicate that aloft layers did not significantly alter ground level concentrations and Monday's fresh nitrogen oxide emissions significantly reduced ground level ozone concentrations. The low R^2 may indicate a total exhaustion of aloft profiles as they existed the day before. Both phenomena indicate that on Mondays, unlike other days of the week, when ozone concentrations suffer significant decreases, carryover is absent. In a similar analysis of increases of 20 ppbV or more, they are well spread through all days of the week with R^2 values varying widely (0.14 to 0.85) but they are never very low

(0.01 to 0.03). Decreases in ground level ozone concentrations show influence of carryover manifested in either ozone aloft profiles not changing at all from day to day or changing significantly. Increases in ground level ozone concentrations show a more variety of changes in ozone aloft profile. Carryover seen in strong or weak correlations between ozone aloft profiles has a day-of-the-week influence. Moreover, ground level ozone concentrations decline more significantly in the absence of contribution from ozone aloft. There are indications that ozone aloft profile has a day-of-the-week relationship and that the absence of carryover is related to significant reductions in ground level ozone concentrations.

LANM Peak							
Week	Fri	Sat	Sun	Mon	Tue	Wed	Th
3-Jul	102	87	98	46	45	46	48
10-Jul	35	37	56	44	40	44	60
17-Jul	43	39	46	51	22	56	40
24-Jul	50	46	57	49	41	55	58
31-Jul	61	85	96	82	90	59	52
7-Aug	46	38	34	34	40	54	61
14-Aug	46	37	59		17	33	43
21-Aug	56	80	87	45	59	70	62
28-Aug	60	86	120	86	73	68	73
4-Sep	36	66	64	56	61	58	33
11-Sep	41	56	75	42	32	35	59
18-Sep	29	38	73	81	82	31	3
25-Sep	36	83	111	60	66	68	28
2-Oct	47	59	59	36	31	43	35
9-Oct	30	33	36	40	23	26	
16-Oct	53	56	57				

Table 3. Hourly daily LANM maximum ozone concentrations

These are the preliminary implication of analyses of the data from the first 100 meters of ozone aloft profile at a source site during SCOS97-NARSTO. Continuous aloft data at more sites and for a more significant fraction of the aloft profile would provide a better understanding of carryover. During SCOS97-NARSTO, ozone balloon data provided a snap shot of the entirety of the aloft profile. Looking at these snap shots in view of the evolution of ground level concentrations provides another piece of anecdotal analysis to focus on multi-day carryover events.

In Figure 2, the raw file of ozone balloon data from USC is provided. It is conceptually convenient to separate the closest layer to the ground (up to 500 to 700 meters agl) as the compartment in the atmosphere most susceptible to interaction with the ground-based emissions and atmospheric chemistry associated with these emissions. At night, this reservoir layer may be reduced to very low concentrations due to the loss of daytime atmospheric chemistry, the influence of the nocturnal boundary conditions, and nighttime emissions of nitrogen oxide. During the day, much of ozone buildup related to that day's atmospheric chemistry fills this compartment first. For further convenience we have called this layer the "reservoir."

There are a series of layers of ozone above the reservoir (from 500-700 up to 3,000-4,000 meters AGL) that can be viewed for conceptual convenience as one alpha layer. These layers are influenced by flow of ozone from the reservoir (daytime) and from above the alpha layer and in turn can influence ozone in the reservoir. Ozone concentrations are not significantly reduced at night because nighttime ground deposition and nitrogen oxide emissions have no significant impact on these layers. Thus, alpha layers may exist at high concentrations for several days. Although their interaction with the reservoir and their consequent impact on ground level ozone concentrations depend entirely on meteorological factors, the ozone concentration load they contain depends entirely on reservoir ozone formation processes that occurred one or several days before.

It is important to keep in mind the three-dimensional nature of ozone layers aloft in the complex southern California Bight where land-sea interactions play a critical role in developing regional meteorology and atmospheric chemistry. Designation of these layers is only for convenience and cannot reflect the full complexity of ozone aloft phenomena. Moreover, data on mixing heights for the USC site need to be further developed to further understand the interaction of these aloft ozone layers.

Nevertheless, the evolution of one of these layers in a series of these snapshots of ozone aloft profile is indicative of interaction of the alpha layers with ground levels; these interactions are noted for the August 22 to 23 high ozone episode shown in Figure 3a to 3f (Friday to Saturday). By the early morning hours (0200) before Saturday, August 23rd, the alpha layer has perhaps 60 to 80 ppbV of ozone within it while the reservoir is essentially exhausted. While the reservoir grows by atmospheric chemistry of morning emissions (0800 hours snapshot), boundary conditions ripen to permit more mixing and by 1400 hours full mixing of the alpha layer with the reservoir is indicated. There are indications that carryover affected the ground level concentrations.

Evolution of the high ozone episode from September 4 (Thursday) to 6 (Saturday) as reviewed through the lens of these snapshots indicates that such carryover can take place over more than one day (Figures 4a to 4h). A narrow alpha layer containing roughly 80 ppbV of ozone began on Thursday and was reinforced during Thursday, existed during Friday and weakened somewhat but did not mix down, and finally mixed down on Saturday and was entirely exhausted contributing to a peak of 66 ppbV at LANM. Carryover from Thursday affected Saturday's ground level ozone concentrations.

These limited analyses overlook the fact that aloft photochemistry is rather like ground level processes in that ozone, reactive organic gases, and nitrogen species are part of a complex set of chemical interactions that continue away from emission sources. These limited analyses also ignore the fact that these snapshots are indications of the three-dimensional phenomena that encompasses the entirety of the southern California Bight and includes land-sea interactions and air parcel transport processes. Further assessment of mixing heights close to the ground is necessary for a thorough understanding of the ozone aloft interactions. This assessment is difficult to do because even new continuous remote sensing instruments have their first range gate at 75-100

meters agl. Nevertheless, there is evidence that aloft layers affected ground level concentrations and that such carryover can occur over more than one day.

Conclusions

There are indications that during SCOS97-NARSTO and for a source area, carryover of ozone had day-of-the-week influences and without the effect of carryover, ground level ozone concentrations are usually reduced. There are also indications that aloft layers, some at least 2 days old, affected ground level concentrations.

References

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Blier, W., and Arthur Winer, Analysis of Weekday/Weekend Differences in Ambient Air Quality and Meteorology in the South Coast Air Basin, Air Resources Board Contract No. 95-334, June, 1999

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Ozone Aloft Profile

USC 080408 15-sec Average

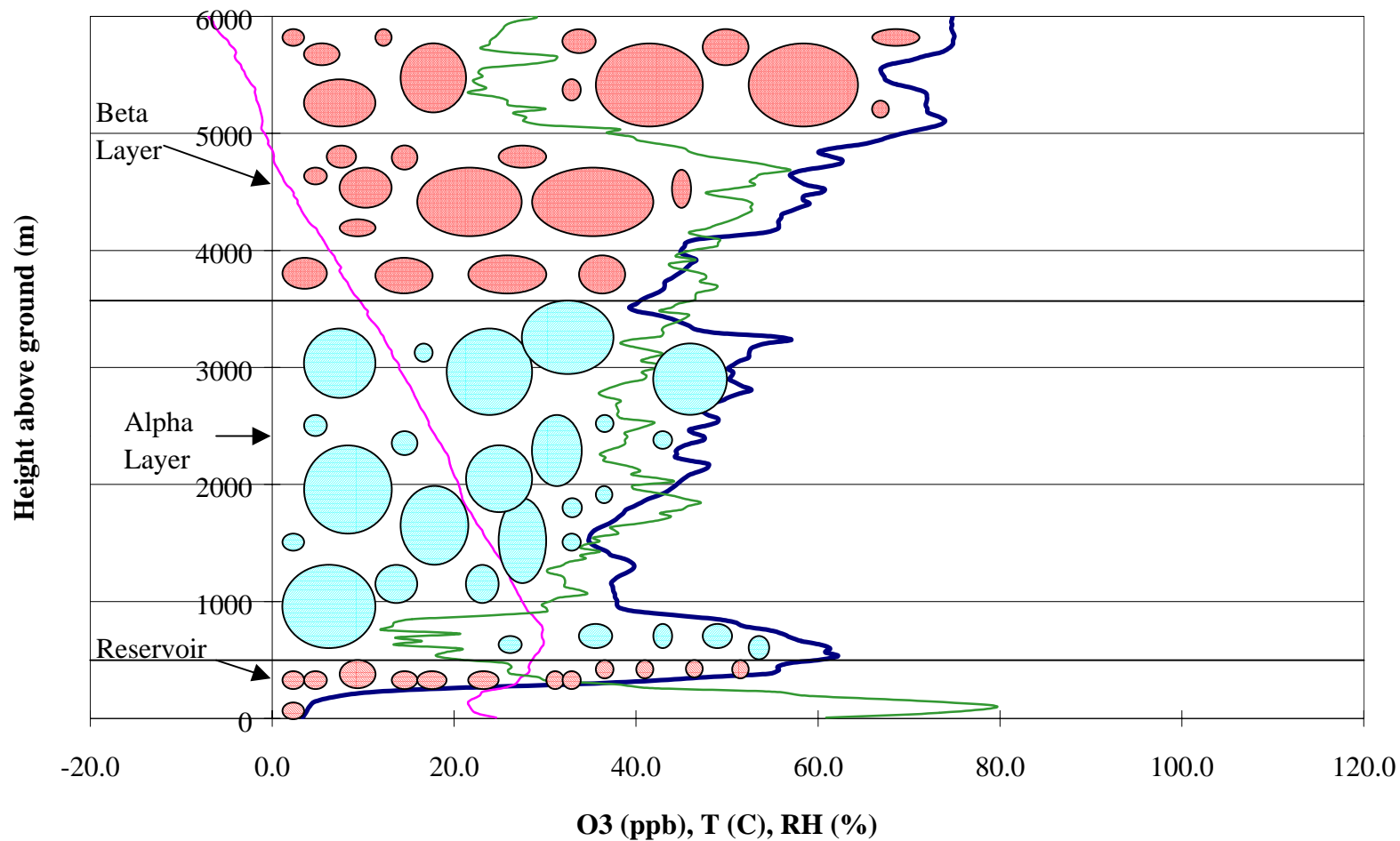
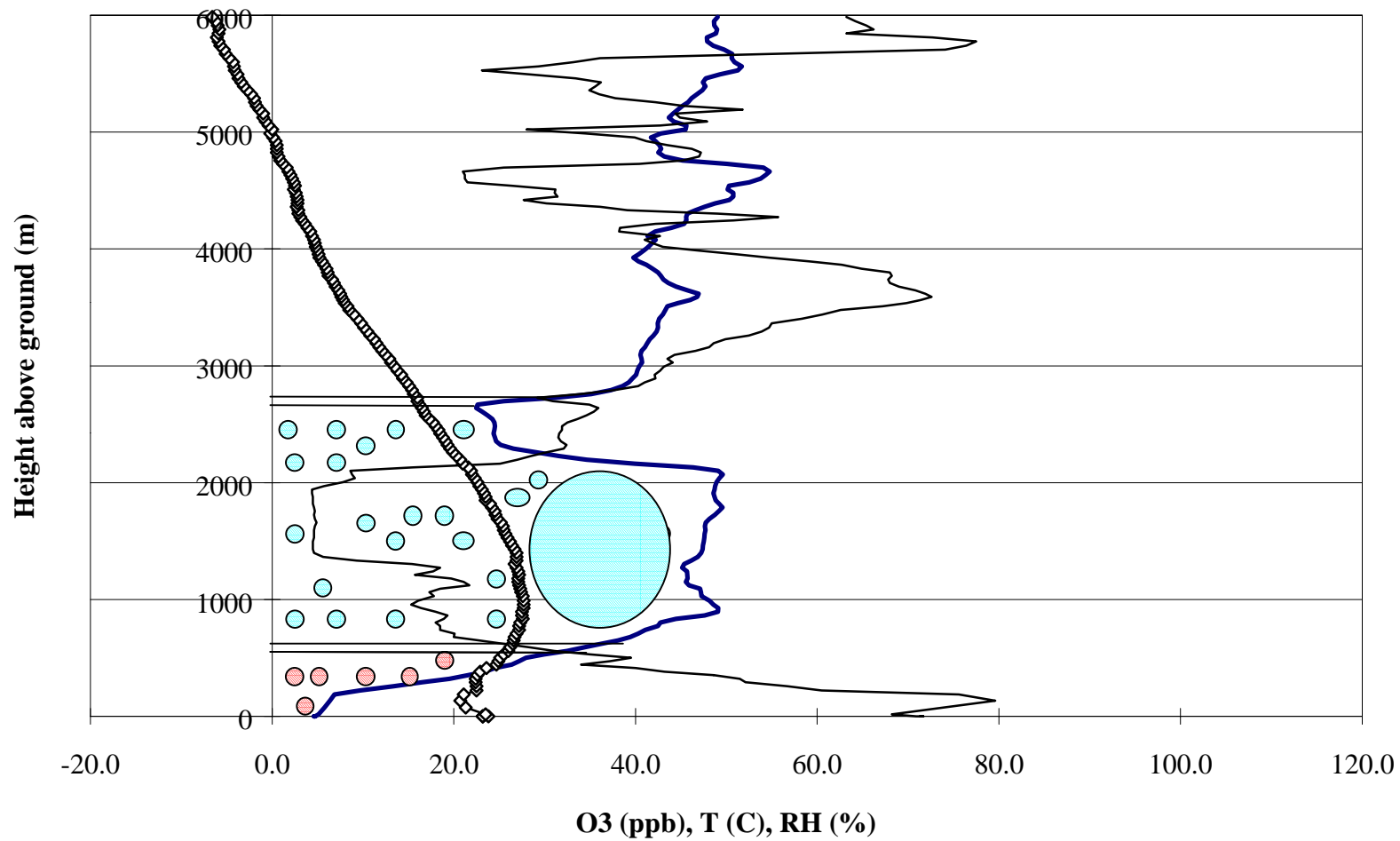


Figure 2. Ozone Balloon Data on August 4, 1997 at 0800 hours Pacific Standard Time (Raw Files)

Ozone Aloft Profiles

USC 082208



Ozone Aloft Profiles USC 082208

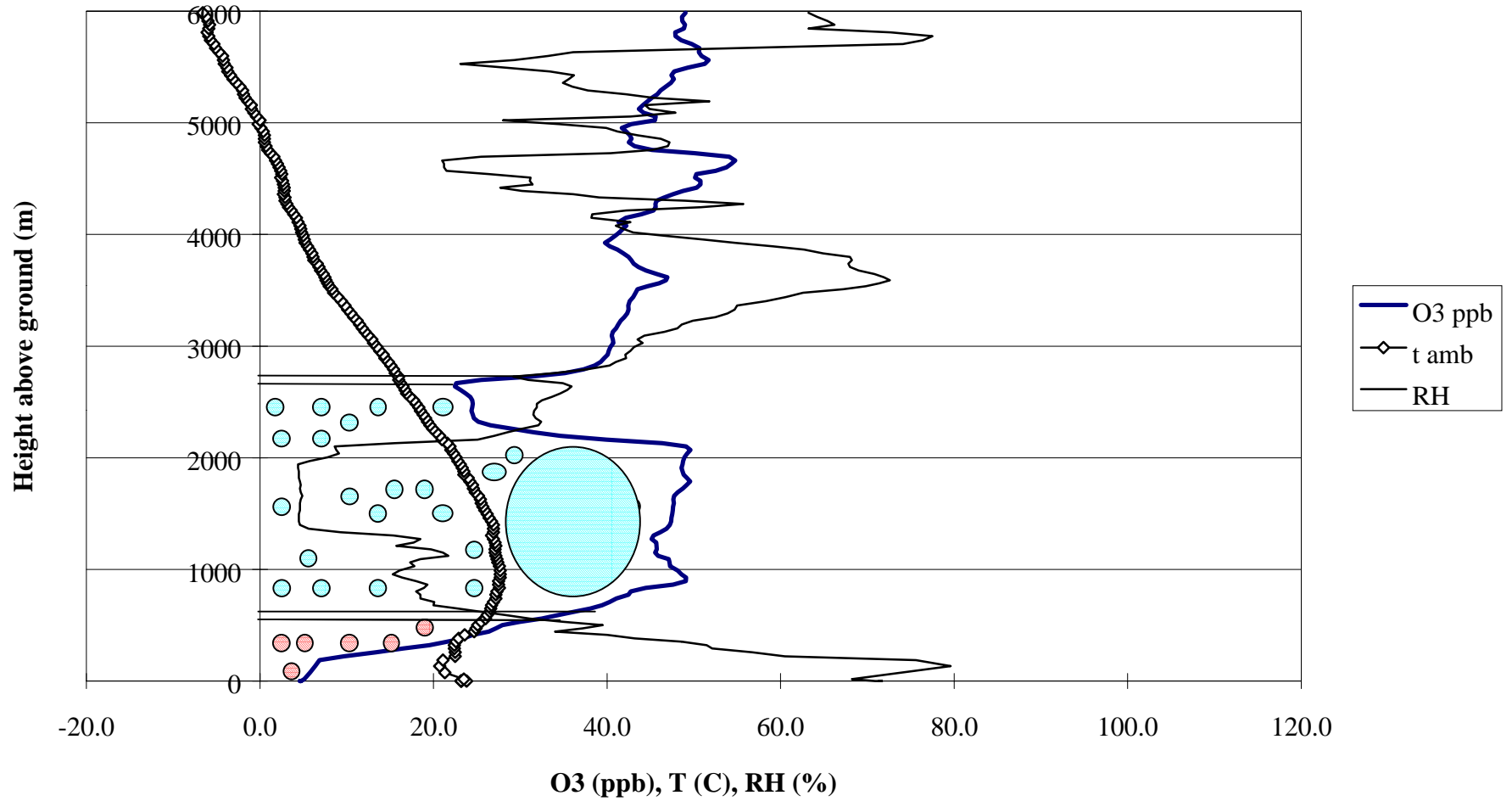


Figure 3a.
not significant

August 22nd Friday at 0800 PST Ozone concentrations in the Reservoir are very low and alpha layer is deep but

Ozone Alfot Profile USD 082214

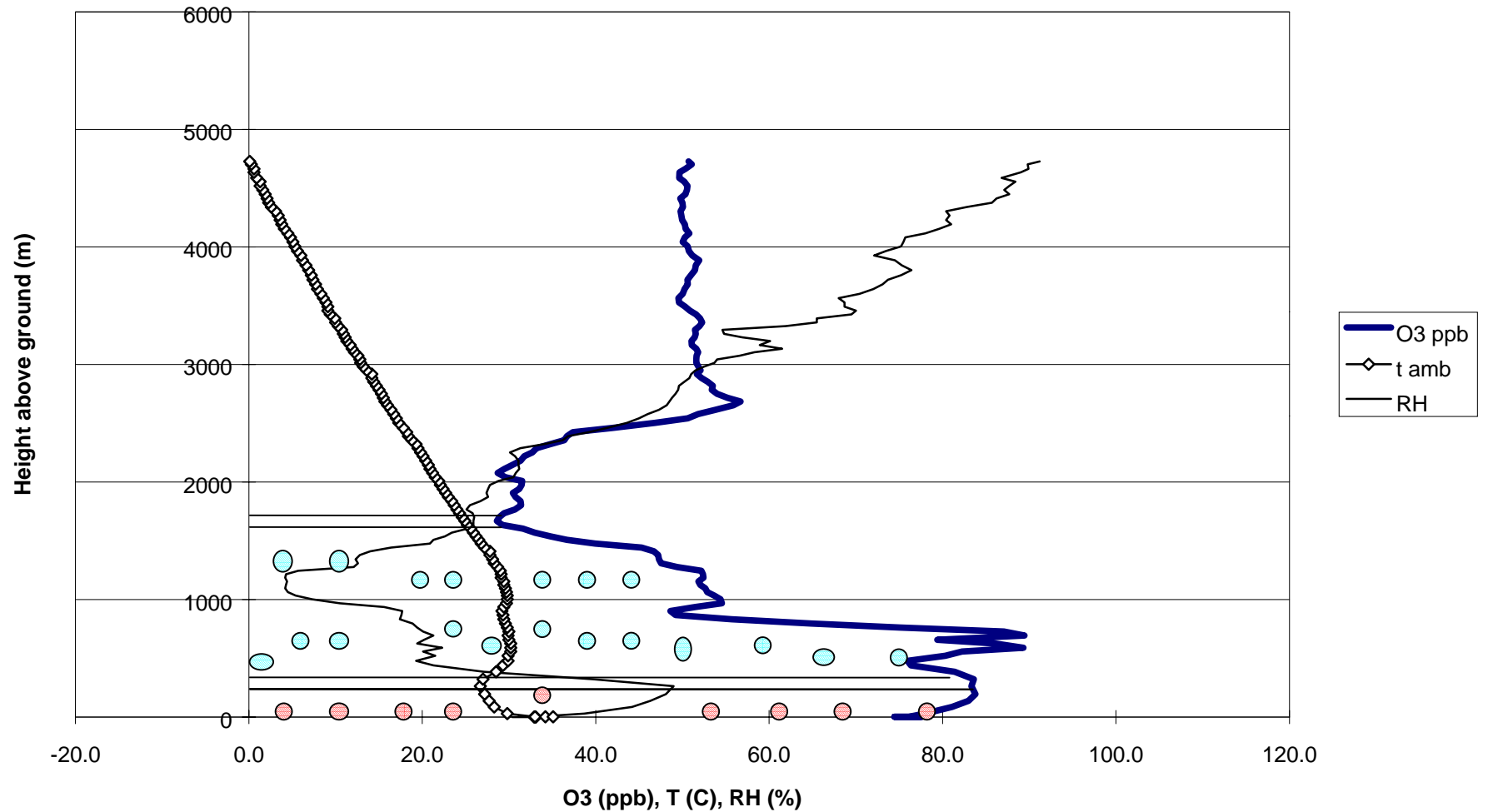


Figure 3b. August 22nd Friday at 1400 PST - ozone photo chemistry is filling the Reservoir and alpha layers. LANM maximum ground level reflects the bottom part of the reservoir depleted by titration (56 ppbV)

Ozone Aloft Profile USC 082220

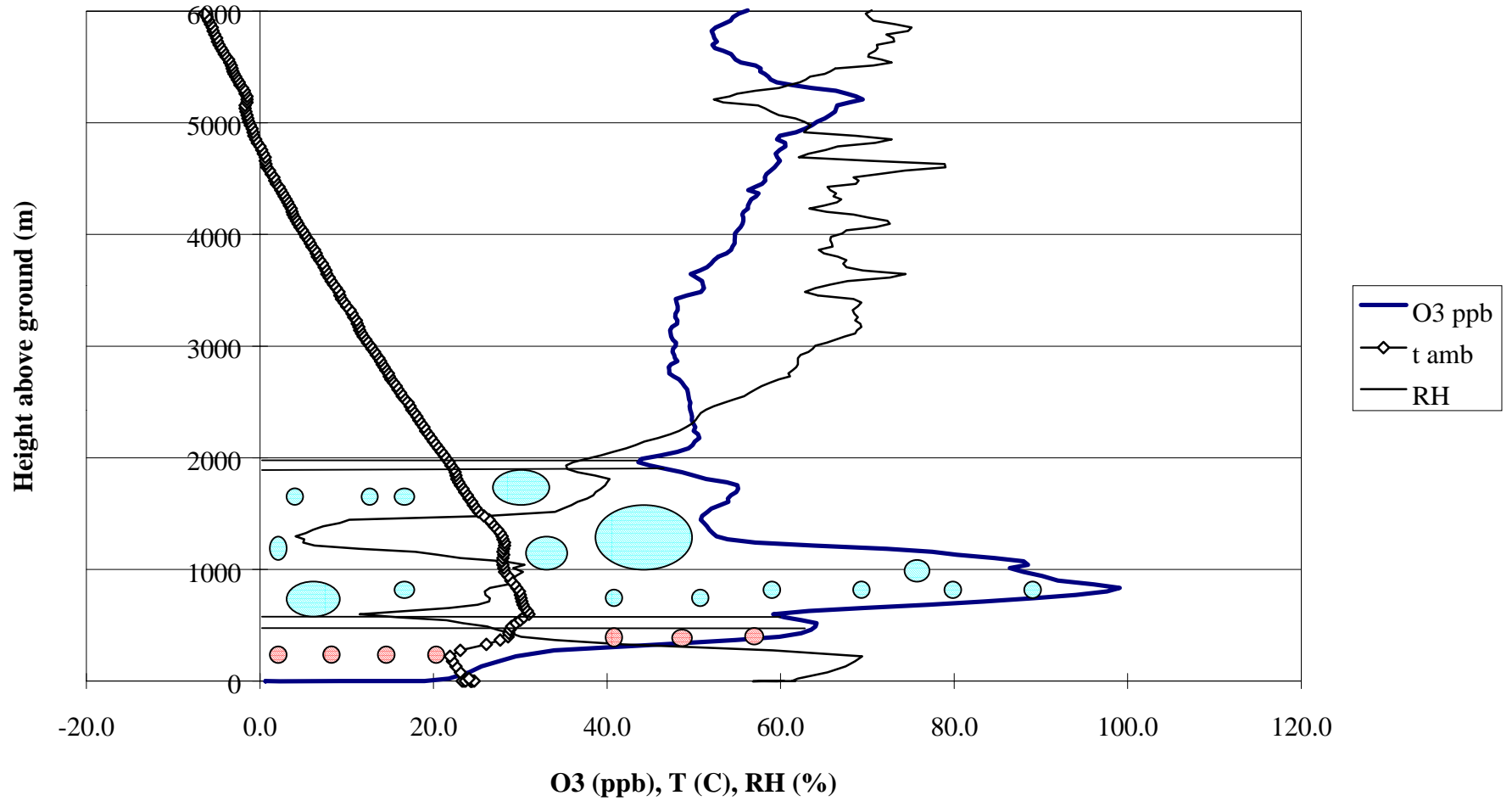


Figure 3c. August 22nd Friday at 2000 PST - Ozone photo chemistry is cut-off and Reservoir is depleted but the alpha layer is separated and remains strong

Ozone Aloft Profile USC 082302

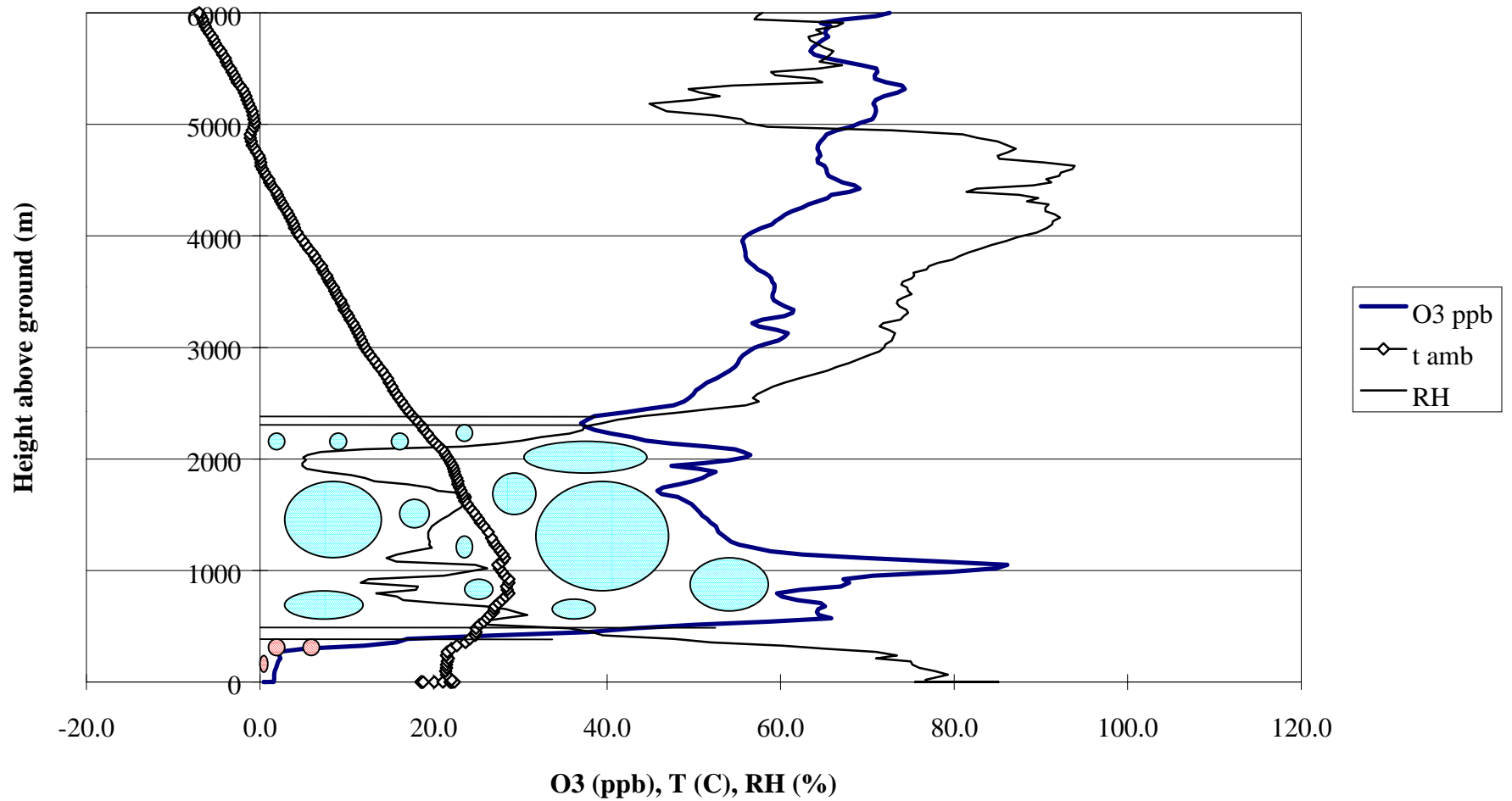


Figure 3d. August 23, Saturday at 0200 Reservoir is non-existent and alpha layer widens and weakens somewhat

Ozone Aloft Profile USC 082308

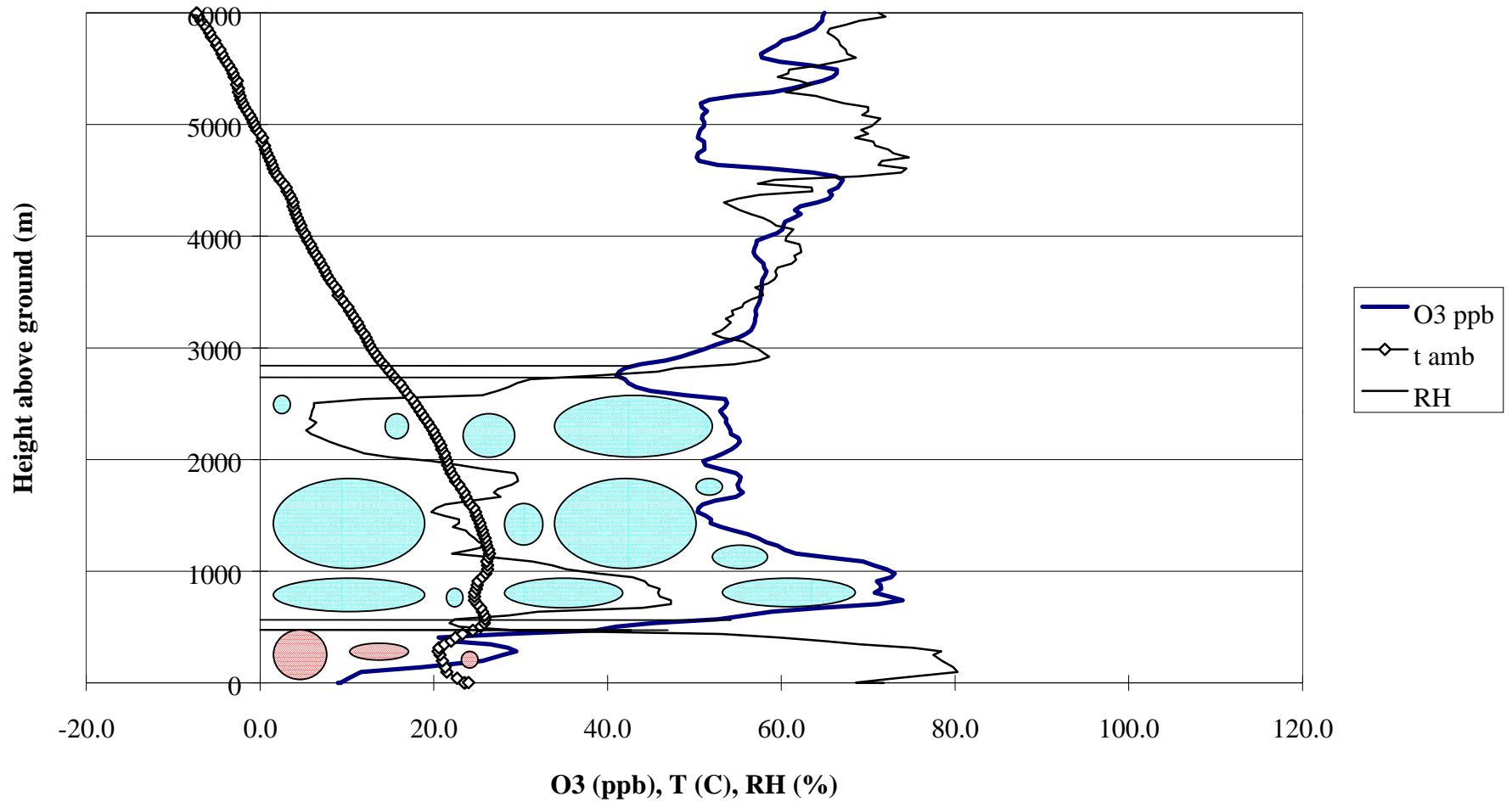


Figure 3e. August 23 Saturday a 0800 hours - ozone photo chemistry is filling the reservoir and alpha layer widens and weakens somewhat but still has around 80 ppbV of ozone

Ozone Aloft Profile USC 082314

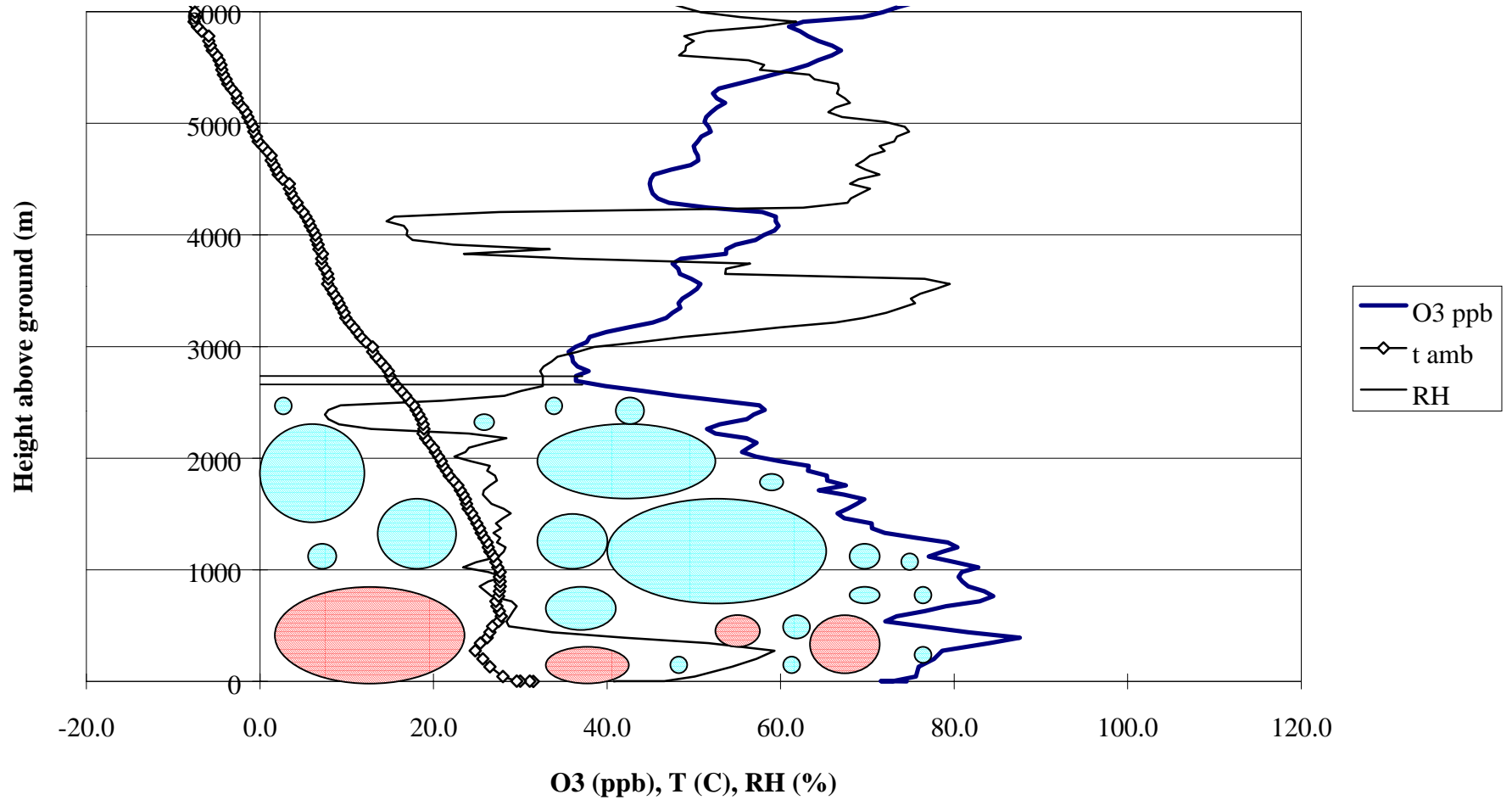


Figure 3f. August 23 Saturday at 1400 hours -Alpha layer has mixed downwards. There is roughly 80 ppbV of ozone up to 1500 meters above ground level. Alpha layer affected LANM maximum ozone ground level (80 ppbV). **Carryover affected ground level ozone.**

Ozone Aloft Profile USC 090408

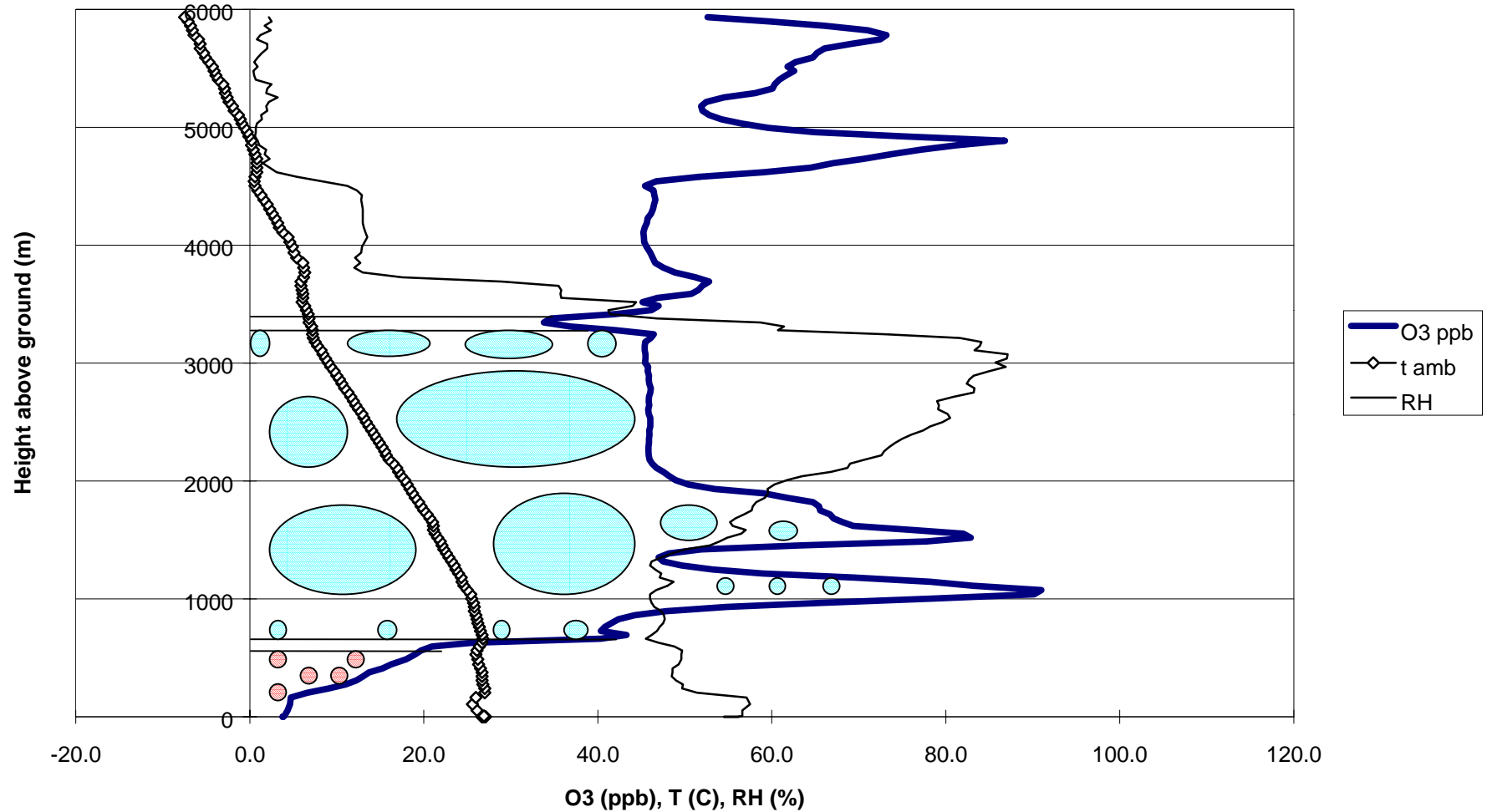


Figure 4a. September 4th Thursday at 0800 - Almost no reservoir exists. Strong and deep alpha layer with around 85 ppbV peak of ozone

Ozone Aloft Profile USC 090414

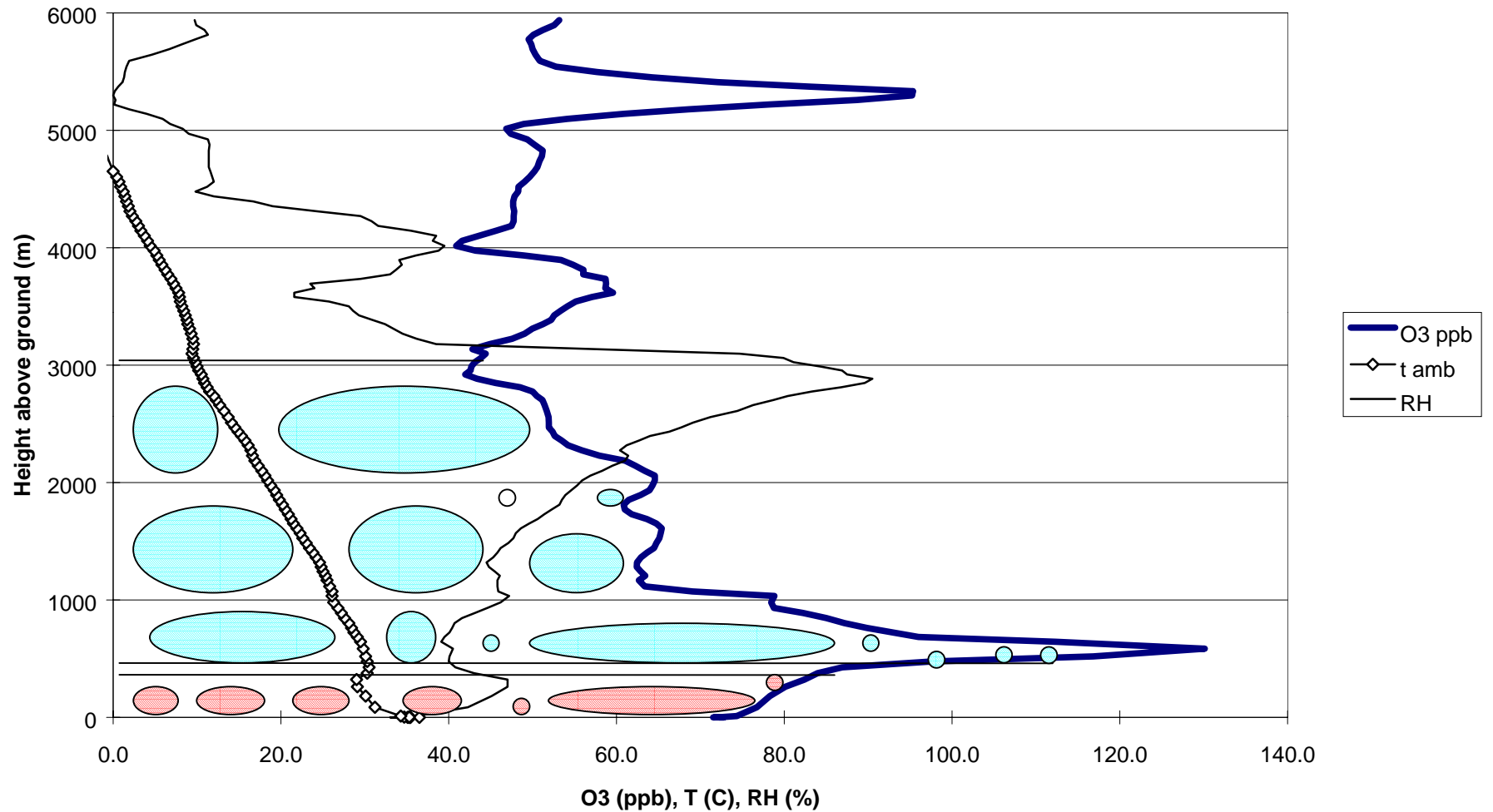


Figure 4b. September 4th Thursday at 1400 hours - Reservoir expanded due to photo chemistry. And alpha layer increased due to photo chemistry to over 120 ppbV peak. Photo chemistry strong enough for a 73 ppbV maximum at LANM

Ozone Aloft Profile USC 090420

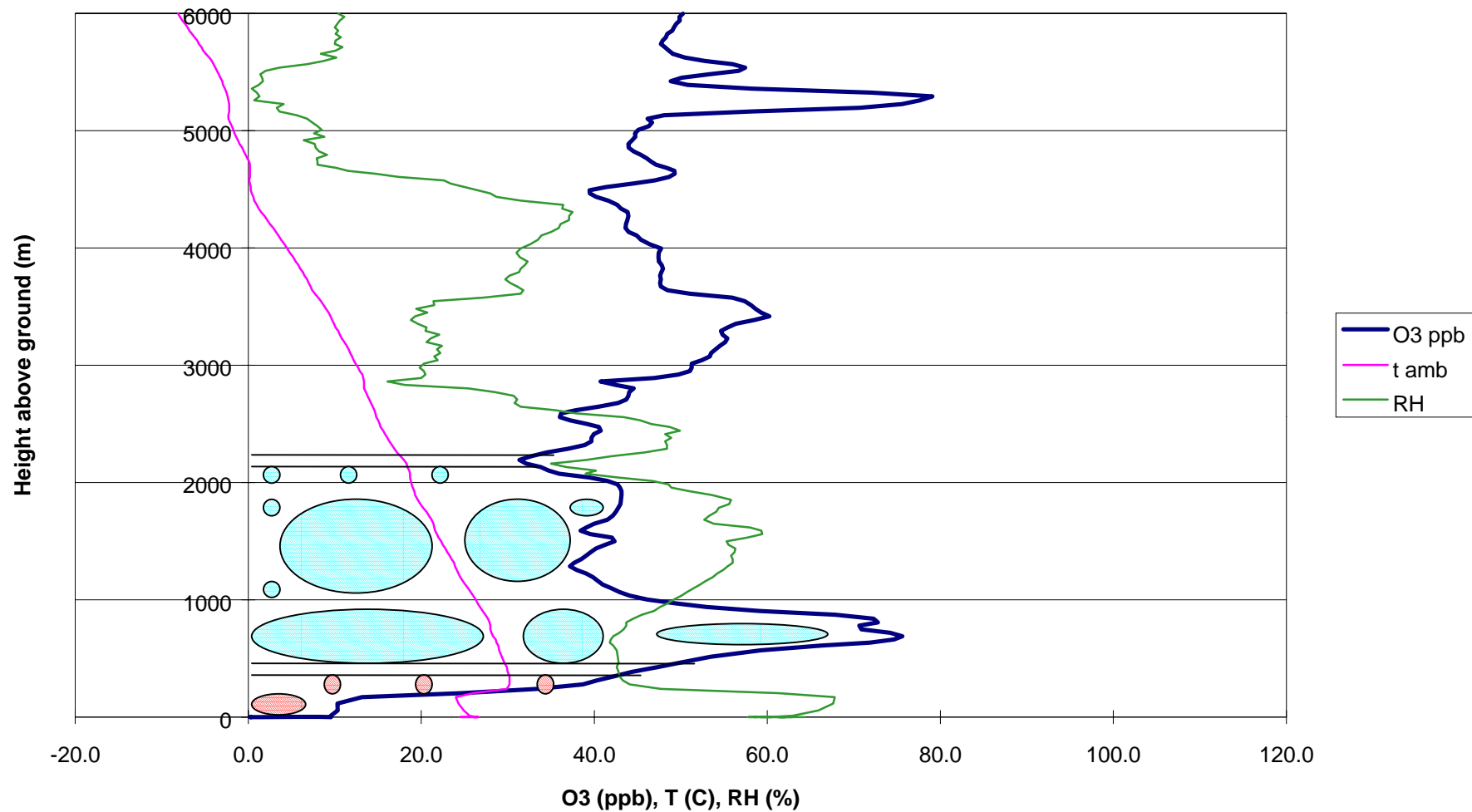


Figure 4c. September 4th Thursday at 2000 hours - Reservoir declined due to loss of photo chemistry. Alpha layer a bit weakened but still with around 80 ppbV peak

Ozone Aloft Profile USC 090502

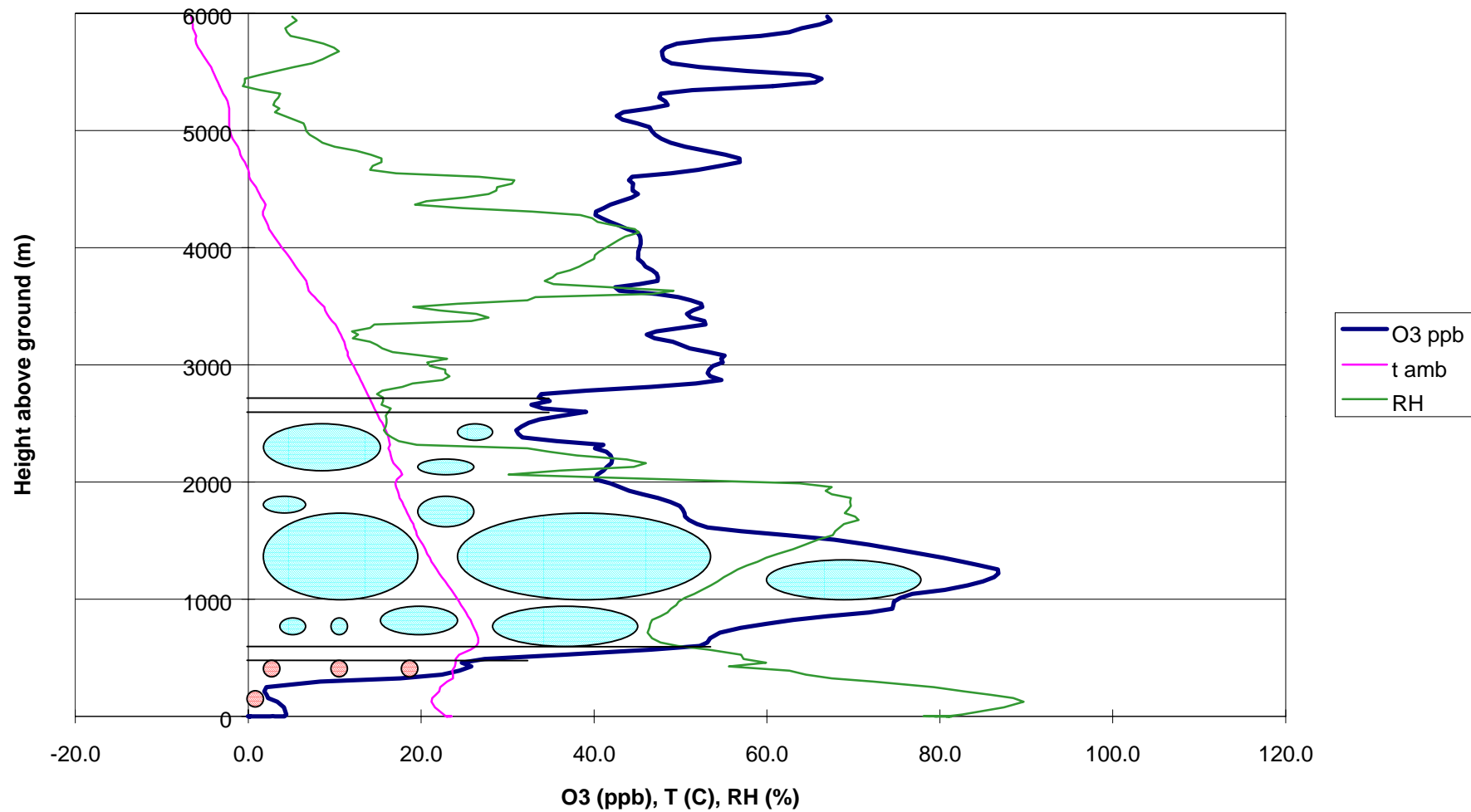


Figure 4d. September 5th Friday at 0200 hours - Reservoir is almost gone. Alpha layer exists with peak around 85 ppbV

Ozone Aloft Profile USC 090514

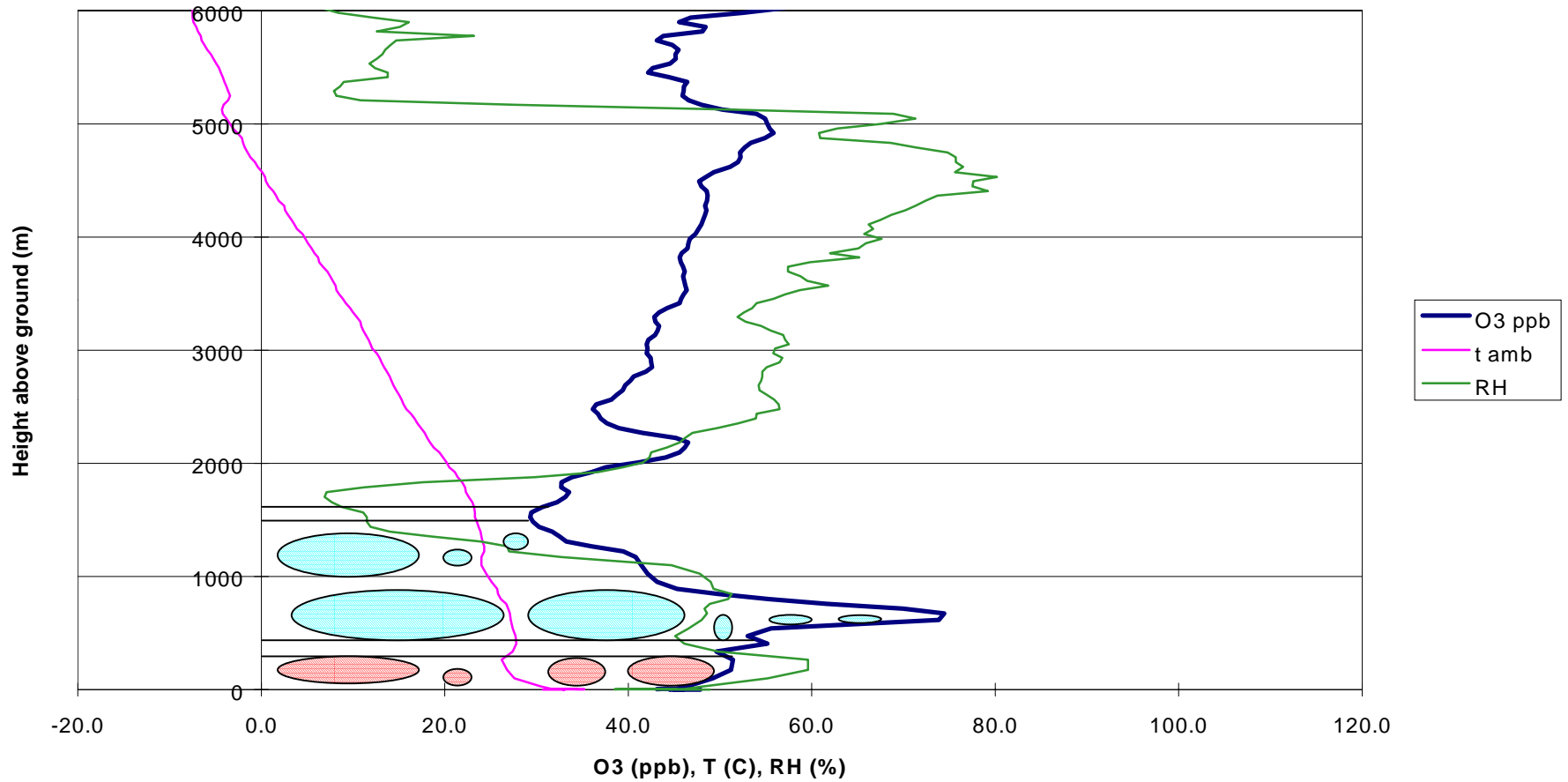


Figure 4e. September 5th Friday at 1400 hours - Reservoir revives due to photo chemistry. Alpha layer is moving down but is not mixing and peak is around 75 ppbV. LANM maximum peak is 36 ppbV consistent with the lower reservoir readings. Alpha layer does not interact with the reservoir or the ground level ozone concentrations. **Carryover from the day before does not impact the ground level ozone concentrations the day after but remains aloft nevertheless.**

Ozone Aloft Profile USC 090602

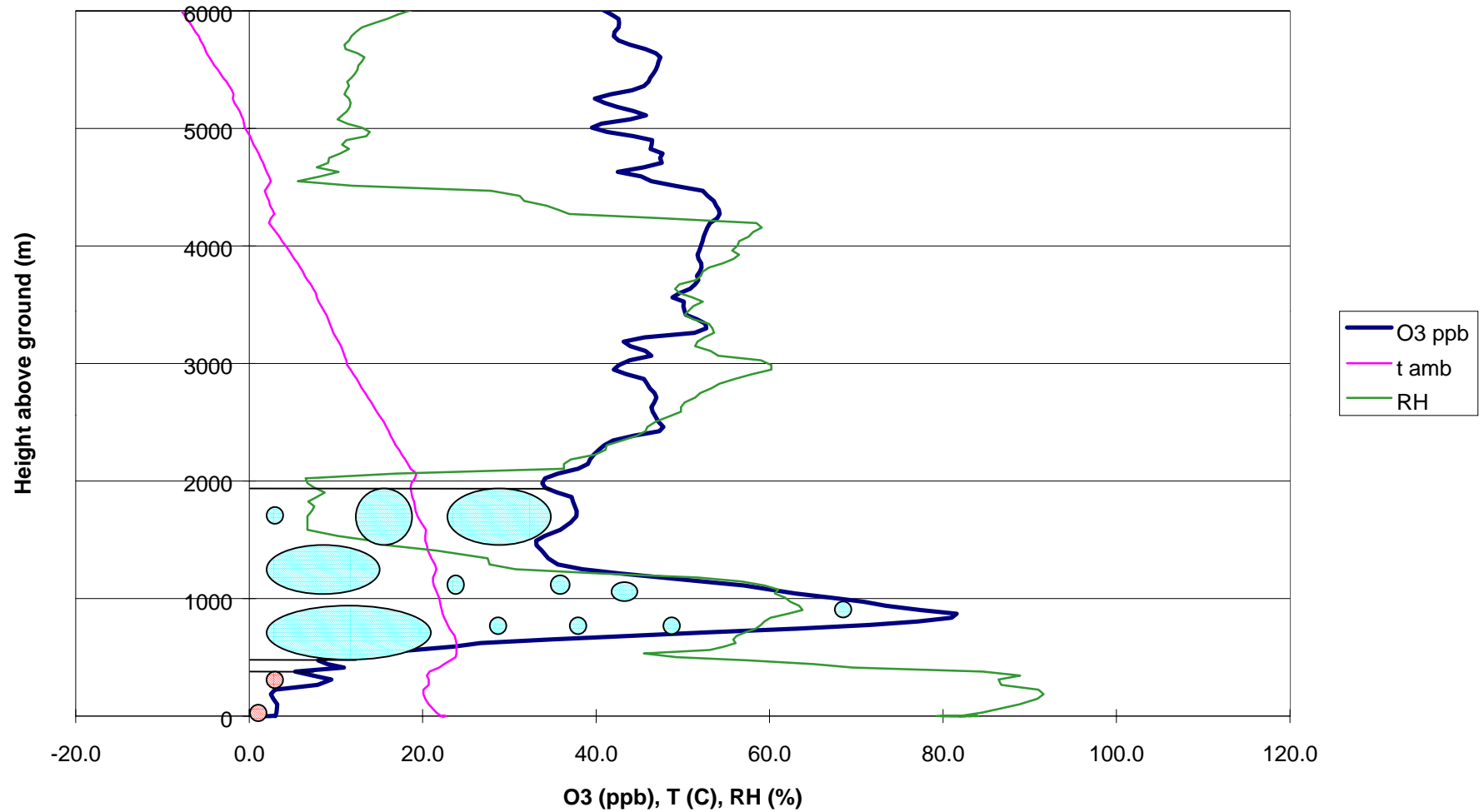


Figure 4f.
1000 meters agl.

September 6th Saturday at 0200 hours - Reservoir is gone. Alpha layer peak remains at 75 ppbV and rose to

Ozonesonde Profile LA090608

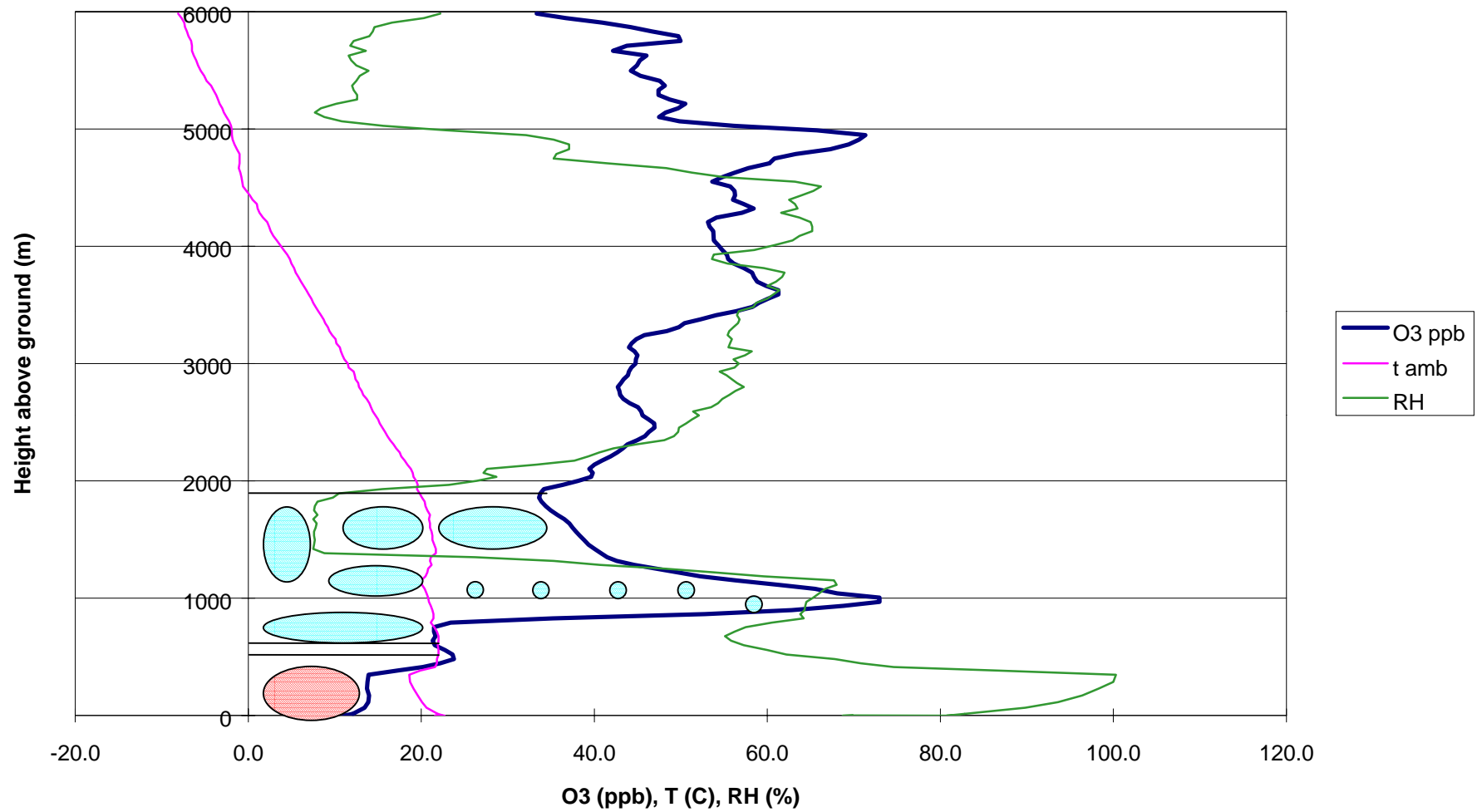
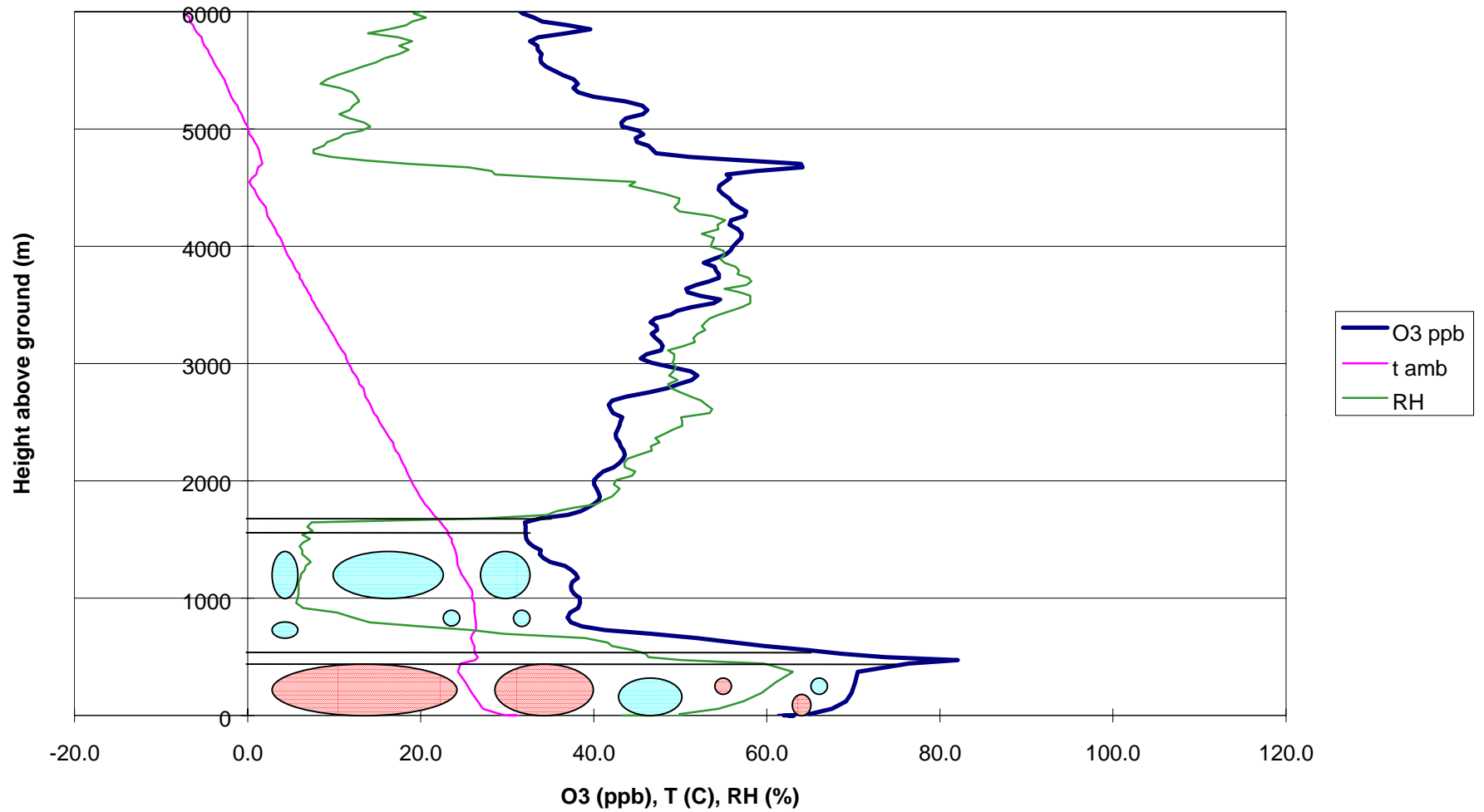


Figure 4g. September 6th Saturday at 0800 hours - Reservoir builds due to photo chemistry. Alpha layer weakened to 75 ppbV and peak rose slightly.

Ozone Aloft Profile USC 090614



Ozone Aloft Profile USC 090614

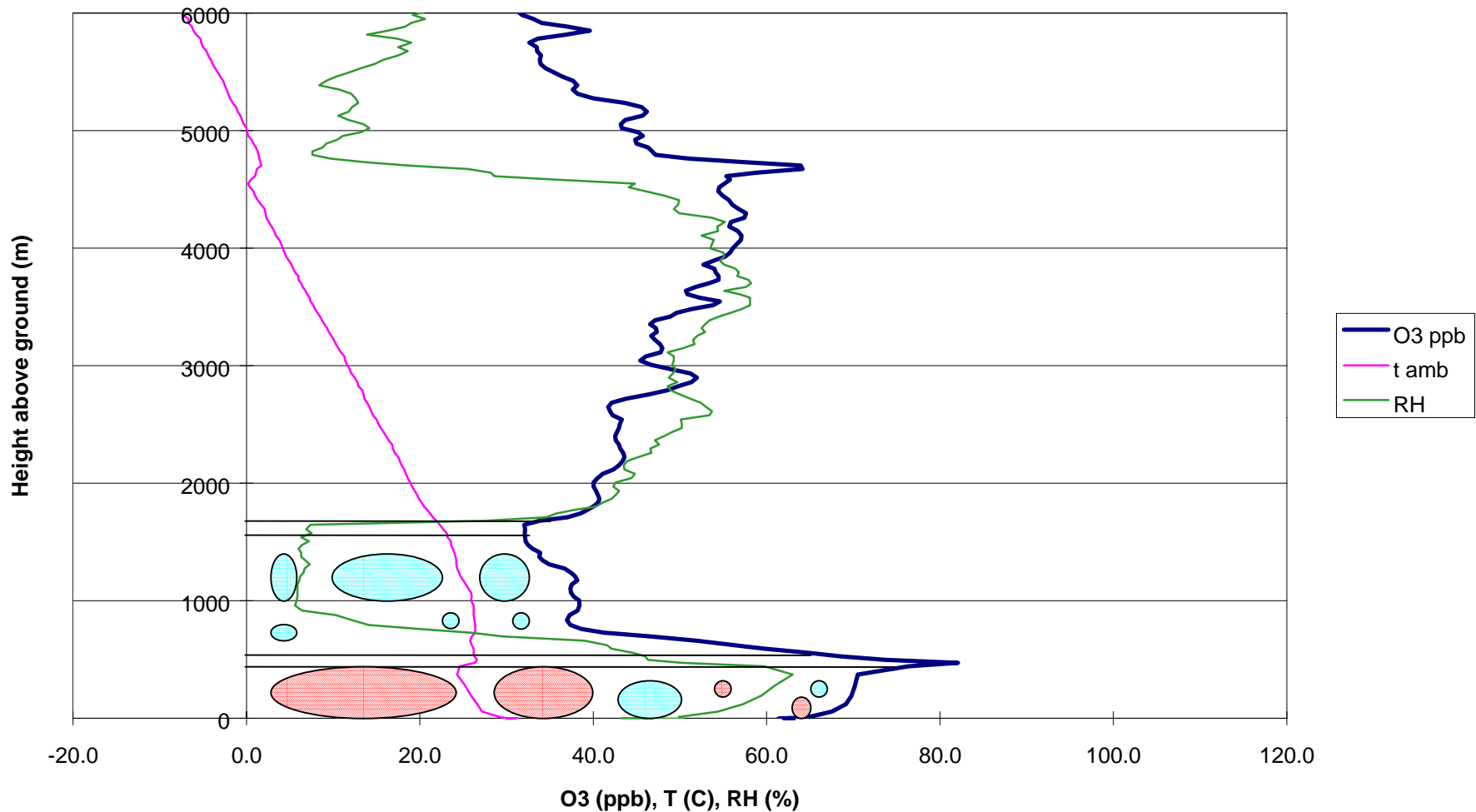


Figure 4h. September 6th Saturday at 1400 hours - Reservoir expanded due to alpha layer mixing down and photo chemistry. Alpha layer was at this time 2-days old and it is now entirely used up. **Carryover from the two days before affected ground level ozone concentrations**